

# (12) UK Patent Application (19) GB (11) 2 091 294 A

(21) Application No 8200158

(22) Date of filing 5 Jan 1982

(30) Priority data

(31) 56/005805

(32) 16 Jan 1981

(33) Japan (JP)

(43) Application published  
28 Jul 1982

(51) INT CL<sup>3</sup>

C22C 5/02

(52) Domestic classification

C7A B249 B279 B289

B309 B319 B320 B325

B327 B329 B32Y B33X

B349 B369 B389 B399

B419 B439 B459 B489

B519 B528 B52Y B531

B533 B535 B537 B539

B53X B549 B559 B610

B611 B612 B616 B619

B620 B621 B624 B627

B62X B630 B635 B63Y

B661 B663 B665 B667

B669 B66X B670

(56) Documents cited

GB 2047749A

GB 1021546

(58) Field of search

C7A

(71) Applicants

Citizen Watch Company

Limited,

No. 1—1, 2-chome,

Nishishinjuku, Shinjuku-

ku, Tokyo, Japan

(72) Inventor

Tsuneji Takasugi

(74) Agents

Marks & Clerk,

57—60 Lincoln's Inn

Fields, London WC2A 3LS

(54) Pink-tinted gold alloy

(57) A gold alloy, consists of gold, from 85 to 95 per cent by weight, a material consisting of palladium, nickel, chromium or a combination thereof, from 2 to 10 per cent by weight, and copper, from 2 to 8 per cent by weight. The alloy may be used for jewellery, spectacle frames or watch cases.

BEST AVAILABLE COPY

GB 2 091 294 A

# **SPECIFICATION**

## **Pink-tinted gold alloy**

This invention relates to a pink-tinted gold alloy which has a high corrosion resistance.

There are varieties of gold alloy which serve as watch cases, bracelets and eyeglass frames, or as decorative precious metals for rings and broaches and the like. It has been conventional practice to use gold alloys having a gold, white or pink color tone. It has been known to add nickel (Ni) or zinc (Zn) to a ternary alloy (Au-Ag-Cu alloy) of gold (Au), silver (Ag) and copper (Cu) for producing the gold alloy having a pink color tone.

The conventional Au-Ag-Cu alloy, in terms of its chemical properties, has a poor corrosion resistance and a poor sulfur resistance, and is therefore disadvantageous in that the original luster and color tone cannot be maintained for long periods of use. Specifically, the decline of corrosion resistance is caused by the high ratio of the Ag and Cu content in the prior art.

The present invention seeks to overcome the above-mentioned problem encountered to the prior art.

According to this invention there is provided a pink-tinted gold alloy consisting of gold, from 85 to 95 per cent by weight; a material selected from the group consisting of palladium, nickel, chromium and a combination thereof, from 2 to 10 per cent by weight; and copper, from 2 to 8 per cent by weight.

The gold alloy composition of the present invention is 85 to 95% Au, 2 to 10% Pd, Ni, Cr or a combination thereof, and 2 to 8% Cu, in terms of per cent by weight. These contained elements all form 100% solid solutions in the combinations Au-Pd, Au-Cu, Pd-Cu and exhibit excellent workability such as ductility and extensibility. Owing to the substitution of Pd, Ni or Cr for the Ag and to the greatly diminished Cu content, an excellent corrosion resistance is obtained, and a bright and extremely attractive pink tint is achieved.

The Au content is 85 to 95% by weight for providing a high-quality gold alloy. The Pd, Ni and Cr do not diminish corrosion resistance as mentioned above, and are effective in adjusting the color tone of the gold alloy of the present invention, thereby providing the gold alloy with a soft pink tint. When the Pd, Ni and Cr, solely or in combination, is less than 2% by weight, the color tone becomes too dark so that a bright, soft tint cannot be obtained. When the percentage of Pd, Ni, Cr or a combination thereof exceeds 10% by weight, the whiteness of the color tone is intensified so that a noble pink tint cannot be obtained. Accordingly, the Pd, Ni or Cr content, or a combination thereof, is set to from 2 to 10% by weight. Cu is the most effective element for achieving the pink tint. When the Cu content is made small, the color tone approaches the color of gold. When the Cu content is made large, the color tone takes on the reddish color of copper. With a low content of less than 2% by weight, the color tone of the gold alloy of the present invention approaches the color of gold, and with a Cu content of greater than 8% by weight, the color red is intensified, so that the noble and highly attractive pink tint cannot be obtained. The Cu content therefore is set to from 2 to 8% by weight.

Next, the present invention will be described on the basis of examples thereof.

### **EXAMPLE NO. 1**

	Au	Pd	Cu	Ni	Cr	Color Tone
Alloy (1)	85	10	5	—	—	Pale pink gold
Alloy (2)	85	7	8	—	—	Red copper-tinted pink gold
Alloy (3)	90	7	3	—	—	Pale pink color
Alloy (4)	90	2	8	—	—	Red copper-tinted (intense) pink gold
Alloy (5)	92	5	3	—	—	Pink gold
Alloy (6)	95	3	2	—	—	Gold-tinted pink gold
Alloy (7)	90	—	3	7	—	Same color tone as Alloy (3)
Alloy (8)	90	—	3	—	7	Same color tone as Alloy (3)
Alloy (9)	90	3	3	4	—	Same color tone as Alloy (3)

(% by weight)

TABLE I Gold Alloy Components

Each gold alloy having composition shown in Table I is dissolved in an argon gas atmosphere by using a high-frequency induction-heated smelting furnace and is repeatedly heat treated and rolled to produce a sheet having a thickness of 1.5 mm. The heat treatment is in an argon gas atmosphere with the temperature held at 800°C for 45 minutes. Cooling is effected with water as the coolant.

To investigate the characteristics of the gold alloy of the present invention, the sheet is finished to a mirror surface by an ordinary buffing process and then subjected to a tint test and corrosion test.

As shown in Table I, the color tone of the gold alloy of the present invention exhibits a very slight change in accordance with the amount of Pd and Cu added, so that the tint may be readily adjusted as desired.

Next, a corrosion test is carried out. The corrosion test is effected by an artificial perspiration immersion test and a CASS test. The conditions for the perspiration immersion test are as follows:

(1) Liquid composition

sodium chloride (NaCl) 9.9 g/liter

urea ((NH<sub>2</sub>)<sub>2</sub>CO) 1.7 g/liter

lactic acid (C<sub>3</sub>H<sub>5</sub>O<sub>3</sub>) 1.7 g/liter

sodium sulfide (Na<sub>2</sub>S) 0.8 g/liter

ammonium chloride (NH<sub>4</sub>Cl) 0.2 g/liter

sucrose 0.2 g/liter

(2) Liquid temperature

40°C

(3) Immersion time

48 hours

The conditions for the CASS test are as follows:

(Same conditions as Japanese Industrial Standards D 0201)

(1) Liquid composition

sodium chloride (NaCl) 50 g/liter

copper chloride(II) (CuCl<sub>2</sub>) 0.26 g/liter

acetic acid (CH<sub>3</sub>COOH) 1 to 3 milliliter/liter

Acetic acid is applied to the liquid consisting NaCl and CuCl<sub>2</sub> for controlling a value of PH, from 3.0 to 3.1.

(2) The liquid (1) is sprayed toward the sheet in a test bath at a value of pressure 1 kg/cm<sup>2</sup>.

(3) Temperature in the test bath 35°C

(4) Time

The spray (2) is continued for 96 hours. Following these tests, the gold alloy of the present invention is inspected visually for changes in color, for corrosion and for changes in luster. As a result of the artificial perspiration immersion test and the CASS test is found that there is absolutely no occurrence of corrosion and no change in color or in luster. Thus the state originally exhibited by the alloy when it is subjected to the corrosion resistance test is maintained.

In the Example No. 1, it is a main experiment that the element Ag in the conventional Au-Ag-Cu alloy composition is substituted by Pd, but the objects of the present invention can be fully achieved even if Ni or Cr, solely or in combination, is added in place of Ag.

EXAMPLE NO. 2

A sputtering treatment using the gold alloy of the present invention is applied to the surface of a watch dial manufactured by an ordinary method for forming a thin layer on the surface.

In this Example, the gold alloy (5) shown in Table I is utilized for a sputtering target which is set to a cathode.

The sputtering is conducted by introducing argon gas and by holding the pressure at  $3 \times 10^{-2}$  Torr, with the sputtering being effected for five minutes with an applied voltage of 400 V DC. The obtained layer has a thickness of  $1.5 \mu$ .

The watch dial completed by this treatment is such that the composition of the layer obtained by the sputtering treatment and the target composition are almost identical, so that the target color tone and the pink gold color are the same.

Next, the resulting dial is subjected to a corrosion resistance test, based on a moisture test at  $40^{\circ}\text{C}$  for 48 hours, and to a light-resistance test based on a sunshine weathermeter test. The conditions for the sunshine weather meter test are as follows:

(1) The light having wave length substantially equal in wave length of sunshine is continually applied for 150 hours.

(2) Temperature  $63^{\circ}\text{C}$

(3) Humidity 60%

The results are excellent with absolutely no change in corrosion or light resistance.

It is generally known that the color tone of an alloy whose elements have sputter indices that are close to one another is the same as the color tone of the layer by the sputtering treatment. Therefore, when the alloy of the present invention is viewed in this view, it may be understood that the Au-Pd-Cu gold alloy is the optimum target material since the sputtering indices are close to one another, namely  $\text{Au} = 2.40$ ,  $\text{Pd} = 2.08$ ,  $\text{Cu} = 2.35$  (sputter indices with respect to an argon ion energy of 500 eV).

With a gold alloy target in which Ni or Cr is added instead of Pd, color tone of the sputtering layer exhibited a tendency toward a dark pink gold since the Ni sputter index of 1.45 and the Cr sputter index of 1.18 are a little lower than that of Pd.

As described above, the present invention makes it possible to obtain a highly attractive pink-tinted gold alloy with excellent corrosion resistance and workability and exhibits very practical effects, therefore, the gold alloy of the present invention may be applied to external components for watches, to eyeglass frames and to a decorative precious metal. In this utilization, the gold alloy of the present invention is directly used for the external components for watches or the like. However, the gold alloy of the present invention can be used also as a target material for sputtering, and therefore has an extremely wide range of applications.

### CLAIMS

1. A pink-tinted gold alloy consisting of: gold, from 85 to 95 per cent by weight; a material selected from the group consisting of palladium, nickel, chromium and a combination thereof, from 2 to 10 per cent by weight; and copper, from 2 to 8 per cent by weight.

2. A pink-tinted gold alloy substantially as hereinbefore described with reference to the Examples.